

(FILE 'HOME' ENTERED AT 15:41:53 ON 22 APR 2003)

FILE 'CAPLUS, USPATFULL' ENTERED AT 15:42:06 ON 22 APR 2003

L1 35 S BENZYL BROMIDE (P) BROMINE (P) TOLUENE
L2 27 S L1 AND MOLE?
L3 21 S L2 AND GAS?
L4 9 S L3 AND BROMINATION
L5 0 S L4 AND BENZYLIC BROMINATION
L6 1 S L4 AND BENZAL
L7 8 S L4 NOT L6
L8 8 DUP REM L7 (0 DUPLICATES REMOVED)
L9 17846 S BENZYL BROMIDE
L10 4549 S L9 AND BROMINE
L11 3675 S L10 AND TOLUENE
L12 651 S L11 AND BROMINAT?
L13 105 S L12 AND BENZYLIC
L14 103 S L13 AND WATER
L15 31 S L14 AND HBR
L16 28 S L15 NOT L4
L17 27 S L16 AND LIQUID
L18 23 S L17 AND PHASE
L19 23 DUP REM L18 (0 DUPLICATES REMOVED)
L20 0 S BENZYL BROMIDE/P
L21 79 S BENZYL BROMIDE\P
L22 39 S L21 AND BROMINE
L23 34 S L22 AND TOLUENE
L24 34 S L23 NOT L4
L25 5 S L24 AND HBR
L26 179 S BENZYL BROMIDE/TI
L27 14 S L26 AND BROMINE
L28 6 S L27 AND TOLUENE
L29 9 S BENZAL BROMIDE/TI
L30 9 S L29 AND BROMI?
L31 2 S L29 AND TOLUENE
L32 9 S L30 NOT L1
L33 7 S L30 NOT L31

FILE 'CASREACT' ENTERED AT 16:09:06 ON 22 APR 2003

L34 STRUCTURE UPLOADED
L35 0 S L34
L36 9 S L34 FUL

FILE 'REGISTRY' ENTERED AT 16:18:23 ON 22 APR 2003

L37 STRUCTURE UPLOADED
L38 0 S L37
L39 121 S L37 FUL

FILE 'CAPLUS, USPATFULL, CA' ENTERED AT 16:19:49 ON 22 APR 2003

L40 25107 S L39
L41 20359 S L40 AND BROMI?
L42 608 S L40 AND HBR
L43 375 S L42 AND TOLUENE
L44 326 S L43 AND WATER
L45 323 S L44 AND ORGANIC
L46 200 S L45 AND BROMINE
L47 117 S L46 AND GAS
L48 111 S L47 AND PHASE
L49 111 S L48 NOT L4
L50 111 DUP REM L49 (0 DUPLICATES REMOVED)

L51 106 S L50 NOT L19
L52 103 S L51 NOT L24
L53 90 S L52 AND MOLE?
L54 5 S L53 AND BENZYLIC

=> d 134

L34 HAS NO ANSWERS

L34 STR

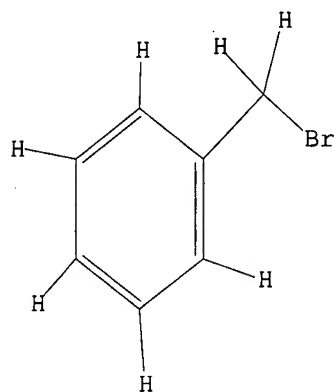
*** STRUCTURE DIAGRAM IS NOT AVAILABLE ***

Structure attributes must be viewed using STN Express query preparation.

=> d 137

L37 HAS NO ANSWERS

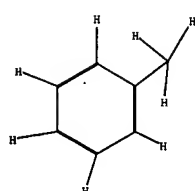
L37 STR



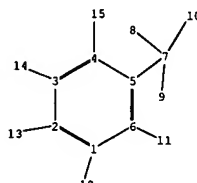
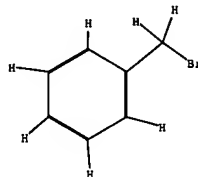
Structure attributes must be viewed using STN Express query preparation.

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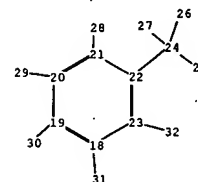
L34



Br-Br



16-17



chain nodes :

7 8 9 10 11 12 13 14 15 16 17 24 25 26 27 28 29 30 31 32

ring nodes :

1 2 3 4 5 6 18 19 20 21 22 23

chain bonds :

1-12 2-13 3-14 4-15 5-7 6-11 7-8 7-9 7-10 16-17 18-31 19-30 20-29 21-28
22-24 23-32 24-25 24-26 24-27

ring bonds :

1-2 1-6 2-3 3-4 4-5 5-6 18-19 18-23 19-20 20-21 21-22 22-23

exact bonds :

1-12 2-13 3-14 4-15 5-7 6-11 7-8 7-9 7-10 16-17 18-31 19-30 20-29 21-28
22-24 23-32 24-25 24-26 24-27

normalized bonds :

1-2 1-6 2-3 3-4 4-5 5-6 18-19 18-23 19-20 20-21 21-22 22-23

Match level :

1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:CLASS 8:CLASS 9:CLASS 10:CLASS
11:CLASS 12:CLASS 13:CLASS 14:CLASS 15:CLASS 16:CLASS 17:CLASS 18:Atom 19:Atom
20:Atom 21:Atom 22:Atom 23:Atom 24:CLASS 25:CLASS 26:CLASS 27:CLASS 28:CLASS
29:CLASS 30:CLASS 31:CLASS 32:CLASS

fragments assigned product role:

containing 18

fragments assigned reactant/reagent role:

containing 16

reaction site bonds:

7-10:XC 16-17:XC

L28 ANSWER 1 OF 6 CAPLUS COPYRIGHT 2003 ACS

AN 1997:773373 CAPLUS

DN 128:75080

TI Substituent effects on the benzylic bond dissociation enthalpy in **benzyl bromides** (C-Br) and tert-butylbenzenes (C-CH₃): a gas phase thermolysis and liquid phase photoacoustic study

AU Laarhoven, Lucas J. J.; Born, Jan G. P.; Arends, Isabel W. C. E.; Mulder, Peter

CS Leiden Institute of Chemistry, Leiden University, Leiden, 2300 RA, Neth.

SO Journal of the Chemical Society, Perkin Transactions 2: Physical Organic Chemistry (1997), (11), 2307-2312

CODEN: JCPKBH; ISSN: 0300-9580

PB Royal Society of Chemistry

DT Journal

LA English

AB The bond dissociation enthalpies in a no. of substituted benzyl bromides have been studied in the gas phase, using the **toluene** carrier technique, and in soln. with photoacoustic calorimetry. Gas phase thermolysis with unsubstituted benzyl bromide gives an abs. C-Br bond dissociation enthalpy (Ed) at 298 K of 255 \pm 4 kJ mol⁻¹. Competition expts. in the gas phase reveal no substituent effect on the value of Ed(C-Br). Gas phase thermolysis with substituted tert-butylbenzenes also shows no effect on the C[z.sbd6]CH₃ bond dissociation enthalpy for p-CN, p-OH and p-But substituents, with a Ed(C-CH₃) value at 298 K of 299 \pm 2 kJ mol⁻¹. In soln., photoacoustic expts. yield no detectable substituent effect for p-CN, p-But and m-CF₃ substitution of the benzyl bromide, in contrast with other reports. With photoacoustic calorimetry a bond dissociation enthalpy of 254 \pm 4 kJ mol⁻¹ has been found for all benzyl bromides studied. A rationale for the absence of a substituent effect on the benzylic bond dissociation enthalpy is provided.

RE.CNT 34 THERE ARE 34 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L28 ANSWER 2 OF 6 CAPLUS COPYRIGHT 2003 ACS

AN 1952:40888 CAPLUS

DN 46:40888

OREF 46:6913b-d

TI The C-Br bond dissociation energy in substituted **benzyl bromides**

AU Leigh, C. H.; Sehon, A. H.; Szwarc, M.

CS Univ. Manchester, UK

SO Proc. Roy. Soc. (London) (1951), A209, 97-110

DT Journal

LA Unavailable

AB The **toluene**-carrier technique was used for the detn. of the C-Br bond dissociation energies in the substituted benzyl bromides: p-, m-, and o-xyllyl bromides; p-, m-, and o-chlorobenzyl bromides; p- and m-bromobenzyl bromides; p- and m-nitrobenzyl bromides; and p- and m-cyanobenzyl bromides. The rate-determ. step of the decomposition of all these

compds. is detd. Differences in the C-Br bond dissociation energies are calcd. and listed for the above substituted benzyl bromides. The effects of substitution on bond dissociation energies are to be attributed to factors different from those affecting the rates of ionic reactions.

L28 ANSWER 3 OF 6 CAPLUS COPYRIGHT 2003 ACS

AN 1951:15477 CAPLUS

DN 45:15477

OREF 45:2729e-h

TI The carbon-bromine bond dissociation energy in **benzyl bromide** and allyl bromide
 AU Szwarc, M.; Ghosh, B. N.; Sehon, A. H.
 CS Univ., Manchester, UK
 SO J. Chem. Phys. (1950), 18, 1142-9
 DT Journal
 LA Unavailable
 AB cf. C.A. 43, 8250e. The pyrolysis of org. bromides in a stream of **toluene** is described as a method for the detn. of the dissocn. energy (D) of the C-Br bond. The technique used makes it possible to discriminate between 2 mechanisms of decompn.: (a) RBr .fwdarw. R + Br, (b) RBr .fwdarw. olefin + HBr. Both benzyl and allyl bromide decomp. according to mechanism (a), the Br atoms reacting readily with **toluene** to give HBr. The rate of the primary dissocn. process was measured by the rate of formation of HBr. It was proved that the thermal decompns. of benzyl and allyl bromide were homogeneous gas reactions obeying 1st-order kinetics. The activation energies were calcd. at 50.5 \pm 2 kcal./mole and 47.5 \pm 2 kcal./mole, and identified with D(C6H5CH2-Br) and D(CH2:CHCH2-Br), resp. The fate of the allyl radical is discussed, and a rough estimate of the activation energy for the reaction CH2:-CHCH2- + C6H5CH3 .fwdarw. CH2:CHCH3 + C6H5CH2- leads to a value of 14-17 kcal./mole. The problem of ionic contribution in the C-Br bonds is discussed. The estn. of the dissocn. energies of the C-Br bonds of various org. bromides is of great interest, since the values for these dissocn. energies, combined with the heats of formation of the relevant bromides in the gaseous state, make it possible to det. the heats of formation of various org. radicals. Furthermore, the latter data in conjunction with the heats of formation of hydrocarbons make possible the calcn. of the various C-H and C-C bond dissocn. energies and the resonance energies of the relevant radicals.

L28 ANSWER 4 OF 6 USPATFULL
 AN 2000:138552 USPATFULL
 TI Method for preparing substituted **benzyl bromides**
 IN Wingert, Horst, Mannheim, Germany, Federal Republic of
 Gotz, Norbert, Worms, Germany, Federal Republic of
 Keil, Michael, Freinsheim, Germany, Federal Republic of
 Muller, Bernd, Frankenthal, Germany, Federal Republic of
 PA BASF Aktiengesellschaft, Ludwigshafen, Germany, Federal Republic of
 (non-U.S. corporation)
 PI US 6133468 20001017
 WO 9906339 19990211
 AI US 2000-462630 20000111 (9)
 WO 1998-EP4485 19980720
 20000111 PCT 371 date
 20000111 PCT 102(e) date
 PRAI DE 1997-19732693 19970730
 DT Utility
 FS Granted
 EXNAM Primary Examiner: McKane, Joseph K.; Assistant Examiner: Murray, Joseph
 LREP Keil & Weinkauff
 CLMN Number of Claims: 6
 ECL Exemplary Claim: 1
 DRWN No Drawings
 LN.CNT 412
 CAS INDEXING IS AVAILABLE FOR THIS PATENT.
 AB Substituted benzyl bromides of the formula I ##STR1## where at least one

substituent R.sup.1-5 is an electron-attracting group such as fluorine, chlorine, **bromine**, C.sub.1 -C.sub.4 -alkoxycarbonyl, cyano or nitro, and the other substituents R.sup.1-5 are hydrogen or methyl,

are prepared by bromination of substituted **toluenes** of the formula II ##STR2## with a brominating agent at from 20 to 95.degree.

C.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L28 ANSWER 5 OF 6 USPATFULL
AN 1999:121623 USPATFULL
TI Method for producing **benzyl bromide** derivatives
IN Takuma, Kenzi, Kashiba, Japan
Kakimizu, Akiko, Nishinomiya, Japan
Kusaba, Tomoyuki, Takarazuka, Japan
PA Sumitomo Chemical Company, Limited, Osaka, Japan (non-U.S. corporation)
PI US 5962723 19991005
AI US 1998-154631 19980917 (9)
PRAI JP 1997-275733 19971008
JP 1997-292316 19971024
DT Utility
FS Granted
EXNAM Primary Examiner: Geist, Gary; Assistant Examiner: Davis, Brian J.
LREP Birch, Stewart, Kolasch & Birch, LLP
CLMN Number of Claims: 6
ECL Exemplary Claim: 1
DRWN No Drawings
LN.CNT 393

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB The method for producing the benzyl bromide derivatives of the formula: ##STR1## wherein R.sub.1 represents a C.sub.1 to C.sub.5 alkyl group, which comprises reacting a 2-methylphenylacetic acid derivative of the formula: ##STR2## wherein R.sub.1 represents the same meaning above, with **bromine** in the presence of an alkali metal salt. In case that R.sup.1 is an ethyl or isopropyl group, the recrystallization of the above reaction product from aliphatic hydrocarbon solution gives the benzyl bromide derivatives efficiently and in high purity.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L28 ANSWER 6 OF 6 USPATFULL
AN 80:11411 USPATFULL
TI Process for the production of substituted benzal and **benzyl bromides**
IN Riethmann, Jean, Rheinfelden, Switzerland
Marti, Franz, Dornach, Switzerland
Somlo, Tibor, Birsfelden, Switzerland
PA Ciba-Geigy Aktiengesellschaft, Basel, Switzerland (non-U.S. corporation)
PI US 4191621 19800304
AI US 1978-945957 19780926 (5)
PRAI CH 1977-11985 19770930
DT Utility
FS Granted
EXNAM Primary Examiner: Williams, Howard S.
LREP Sprung, Felfe, Horn, Lynch & Kramer
CLMN Number of Claims: 13
ECL Exemplary Claim: 1

DRWN No Drawings

LN.CNT 267

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB The invention describes a process for the production of benzal or benzyl

bromides which contain electrophilic substituents in the ortho- and/or para-position, or mixtures thereof, by the side-chain bromination of correspondingly substituted **toluene**, which comprises introducing elementary chlorine, under irradiation with visible light, into a two-phase system consisting of an aqueous phase and an organic phase and containing a correspondingly substituted **toluene**, at least one metal bromide, and a base, and also the compounds obtained by this process.

L31 ANSWER 1 OF 2 CAPLUS COPYRIGHT 2003 ACS

AN 2001:875487 CAPLUS

DN 136:253909

TI Electrochemical reduction of benzyl iodide, **benzal bromide**, and benzal chlorobromide at carbon cathodes in the presence of nitric oxide in acetonitrile

AU Ji, Chang; Peters, Dennis G.

CS Department of Chemistry, Indiana University, Bloomington, IN, 47405, USA

SO Journal of Electroanalytical Chemistry (2001), 516(1-2), 39-49

CODEN: JECHES; ISSN: 0368-1874

PB Elsevier Science S.A.

DT Journal

LA English

AB Cyclic voltammetry (CV) and controlled-potential electrolysis have been employed to investigate the electrochem. redns. of benzyl iodide, benzal bromide, and benzal chlorobromide at glassy carbon cathodes in the presence of nitric oxide (NO) in acetonitrile contg. tetramethylammonium tetrafluoroborate. One irreversible cyclic voltammetric wave, due to cleavage of the carbon-iodine bond, is obsd. for the redn. of benzyl iodide, whereas cyclic voltammograms for the redns. of benzal bromide and benzal chlorobromide exhibit two cathodic waves, arising from sequential cleavage of carbon-halogen bonds. At appropriate potentials, bulk electrolyzes of the three starting compds. involve, resp., the generation of benzyl, bromophenylmethyl, and chlorophenylmethyl radicals which can couple with NO, and the products include benzaldehyde oxime, benzonitrile,

and O-benzyl benzaldehyde oxime, as well as **toluene**, bibenzyl, and cis- and trans-stilbene. Mechanisms for the formation of the various products are discussed and, using CV, we have estd. the concn. of NO in acetonitrile under the extant exptl. conditions.

RE.CNT 28 THERE ARE 28 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L31 ANSWER 2 OF 2 CAPLUS COPYRIGHT 2003 ACS

AN 1958:30261 CAPLUS

DN 52:30261

OREF 52:5477c-f

TI Benzyl and **benzal bromides**

IN Anthony, Wm. C.

PA Upjohn Co.

DT Patent

LA Unavailable

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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PI	US 2813128		19571112	US	
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AB	4-Alkoxy-2-nitrobenzaldehydes, important in the prepn. of pharmacologically active 6-hydroxytryptamines, are obtained by bromination				
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of 4-alkoxy-2-nitrotoluene using agents such as N-bromoimides and N-bromoalkanoamides or Br₂, and hydrolysis of the resulting product.

4-Methoxy-2-nitrotoluene (5 g.), 10 ml. CCl₄, and 4.8 g.

N-bromosuccinimide refluxed 45 min. gave 87.3% 4-methoxy-2-nitrobenzyl bromide (I), m. 62-3.degree.. I (19.5 g.) and 26 g. (CH₂)₆N₄ refluxed 2 hrs. in 58 ml. 50% aq. HOAc and concd. HCl added gave 75.8%

4-methoxy-2-nitrobenzaldehyde (II), m. 90-2.degree.; phenylhydrazone, m. 144.5-6.degree.; 2,4-dinitrophenylhydrazone, m. 214.degree.. II is also prepd. by refluxing the filtrate from the reaction of 4-methoxy-2-nitrotoluene and N-bromosuccinimide with CaCO₃. II, abs. EtOH, MeNO₂,

and

KOH stirred 1.5 hrs. at -8.degree., HCl added and the temp. maintained below -5.degree., the mixt. extd. with Et2O, the ext. concd., and heated

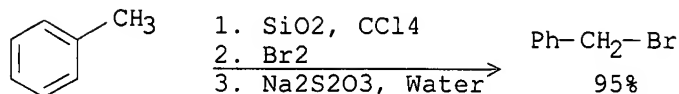
1

hr. with Ac2O and anhyd. NaOAc gave 91.9% 4-methoxy-.beta.,2-dinitrostyrene (III). III in alc. and HOAc warmed with Fe gave 43.2% 6-methoxyindole (IV), m. 91.5-92.degree. IV with oxalyl chloride in

Et2O

gave 6-methoxy-3-indoleglyoxylyl chloride (V), m. 150.degree.. V in dry C6H6 with benzylamine gave 6-methoxy-N-benzyl-3-indoleglyoxamide which with LiAlH4 in tetrahydrofuran formed 6-methoxy-3-(2-benzylaminoethyl)indole (VI). VI dealkylated with AlCl3 produced 6-hydroxy-3-(2-benzylaminoethyl)indole. 4-Ethoxy-2-nitrobenzal bromide, 4-propoxy-2-nitrobenzyl bromide, 4-hexyloxy-2-nitrobenzylbromide and 6-octyloxy-2-nitrobenzal bromide were prepd. similarly to I.

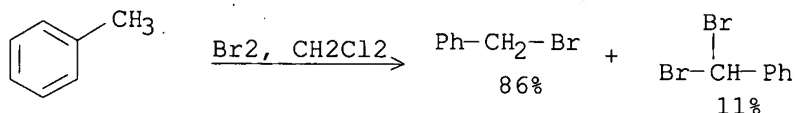
RX(1) OF 16



REF: Bulletin of the Chemical Society of Japan, 74(6), 1151-1152; 2001

AN 135:257004 CASREACT
 TI Increasing the selectivity of bromination of aromatic compounds using Br₂/SiO₂
 AU Ghiaci, M.; Asghari, J.
 CS Department of Chemistry, Isfahan University of Technology, Esfahan, 84154, Iran
 SO Bulletin of the Chemical Society of Japan (2001), 74(6), 1151-1152
 CODEN: BCSJA8; ISSN: 0009-2673
 PB Chemical Society of Japan
 DT Journal
 LA English
 AB In the presence of silica, a no. of arom. hydrocarbons such as toluene, o-, m-, and p-xylene, anthracene and phenol are brominated by Br₂ under mild conditions; for example Br₂/SiO₂ brominates naphthalene readily at 25.degree.C to 1-bromonaphthalene. For comparison, the authors have also brominated all of the substrates with bromine in the absence of silica gel.
 RE.CNT 19 THERE ARE 19 CITED REFERENCES AVAILABLE FOR THIS RECORD
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

RX(1) OF 5



REF: Synlett, (12), 1450-1452; 1997
 NOTE: PHOTOCHEM., USING ZEOLITES MADE IN THE PAPER PROTECTED BENZYLIC POSITION AGAINST BROMINATION

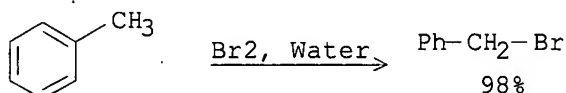
AN 128:127779 CASREACT
 TI Synthesis and application of new phenyl-functionalized zeolites as protection against radical bromination at the benzylic position
 AU Itoh, Akichika; Masaki, Yukio
 CS Gifu Pharmaceutical Univ., Gifu, 502, Japan
 SO Synlett (1997), (12), 1450-1452
 CODEN: SYNLES; ISSN: 0936-5214
 PB Georg Thieme Verlag
 DT Journal
 LA English
 AB Ph-functionalized zeolites were synthesized from PhSi(OEt)₃ and/or

Si(Oet)₄ with dodecylamine as a template at room temp. These zeolites proved to have an ability to protect the benzylic position against radical

bromination. 4-(Chloromethyl)styrene was brominated at the double bond selectively and the benzylic position was intact under irradiation with visible light in the presence of Ph-functionalized zeolites, although without the zeolites, both sites were brominated.

L36 ANSWER 3 OF 9 CASREACT COPYRIGHT 2003 ACS

RX(2) OF 5

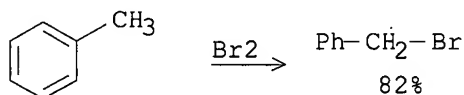


REF: Journal of Organic Chemistry, 62(2), 236-237; 1997

AN 126:89094 CASREACT
TI Free-Radical Bromination of Selected Organic Compounds in Water
AU Shaw, Henry; Perlmutter, Howard D.; Gu, Chen; Arco, Susan D.; Quibuyen, Titos O.
CS Department of Chemical Engineering Chemistry and Environmental Science, New Jersey Institute of Technology, Newark, NJ, 07102, USA
SO Journal of Organic Chemistry (1997), 62(2), 236-237
CODEN: JOCEAH; ISSN: 0022-3263
PB American Chemical Society
DT Journal
LA English
AB The two-phase bromination of toluene, o-, p-, m-xylenes, diphenylmethane, triphenylmethane, and cyclohexane in water using mol. bromine and incandescent light afforded the corresponding free-radical bromination products in high yields. The reactions proceed in the org. phase.

L36 ANSWER 4 OF 9 CASREACT COPYRIGHT 2003 ACS

RX(1) OF 3



REF: U.S., 5449801, 12 Sep 1995
NOTE: photochem.

AN 123:256329 CASREACT
TI Reactive distillation process for free radical halogenation of aromatic and aliphatic compounds
IN Barnum, Chris S.; Blaisdell, Charles T.
PA E. I. Du Pont de Nemours and Company, USA
SO U.S., 9 pp.
CODEN: USXXAM
DT Patent
LA English
FAN.CNT 1

PATENT NO.

KIND DATE

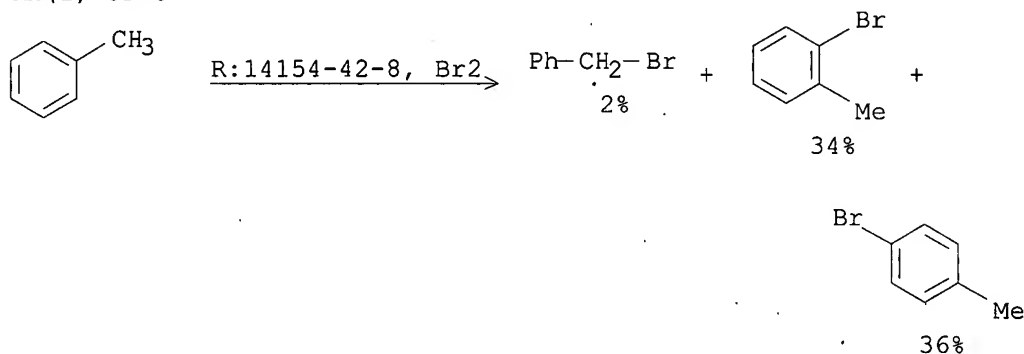
APPLICATION NO. DATE

PI US 5449801 A 19950912 US 1993-91507 19930714
PRAI US 1993-91507 19930714
OS MARPAT 123:256329

AB The title compds. RCY [R = Ac, Si(Cl)mMen, (un)substituted Ph; m = 0-3; n = 0-3; such that m + n = 3; Y = H2X, HX2, X3; X = Cl, Br], useful as (no data) (e.g., benzyl bromide) are prepd. by reacting a vaporized starting material RMe (e.g., PhMe) and X2 (e.g., Br2) in a reaction zone located beneath a condensing zone and above a sepn. zone and collecting the product(s). Photochem. means may be used to conduct the halogenations and app. schematics are presented.

L36 ANSWER 5 OF 9 CASREACT COPYRIGHT 2003 ACS

RX(1) OF 8

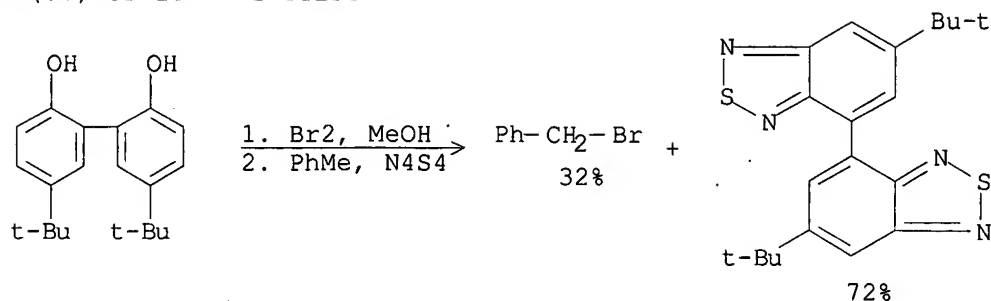


REF: Journal of Chemical Research, Synopses, (1), 28-9; 1990
NOTE: In the dark

AN 113:77766 CASREACT
TI Catalysis by phthalocyanines. Part 35. Chloro(phthalocyanine)aluminium as a catalyst for the nuclear and side-chain halogenation of alkylarenes
AU Kropf, Heinz; Arlt, Brigitta
CS Inst. Org. Chem., Univ. Hamburg, Hamburg, D-2000/13, Germany
SO Journal of Chemical Research, Synopses (1990), (1), 28-9
CODEN: JRPSDC; ISSN: 0308-2342
DT Journal
LA English
AB In the presence of the title compd., bromination of PhMe, p-Me2C6H4, m-Me2C6H4, or mesitylene proceeded at 30.degree. by an electrophilic attack on the arene. At 130.degree. the reaction proceeded by a radical mechanism; the title compd. operates at 30.degree. as a Lewis acid and at 130.degree. as a radical initiator.

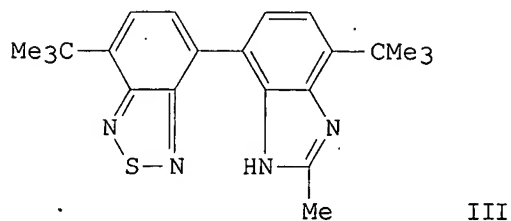
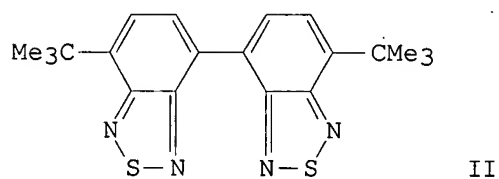
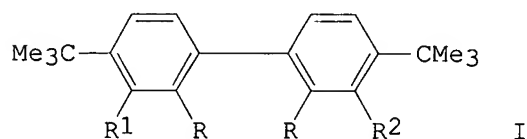
=>

RX(52) OF 187 - 2 STEPS



REF: Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry (1972-1999), (7), 1869-73; 1988

AN 109:190179 CASREACT
 TI Sulfur nitride in organic chemistry. Part 17. Preparation of 1,8-diaminocarbazole
 AU Takahashi, Kazufumi; Eguchi, Hisao; Shiwaku, Sohgo; Hatta, Taizo; Kyoya, Eiji; Yonemitsu, Tadashi; Mataka, Shuntaro; Tashiro, Masashi
 CS Grad. Sch. Eng. Sci., Kyushu Univ., Kasuga, 816, Japan
 SO Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry (1972-1999) (1988), (7), 1869-73
 CODEN: JCPRB4; ISSN: 0300-922X
 DT Journal
 LA English
 GI

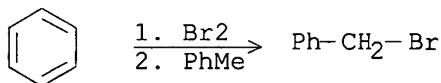


AB Tetrasulfur tetranitride reacted with 5,5'-di-tert-butylbiphenyl-2,2'-diols I (R = OH; R₁ = R₂ = CMe₃, H, Br; R₁ = H, R₂ = Br) to give mixts. of

bi-2,1,3-benzothiadiazol-4-yl (II), benzofurano[3,2-e]-2,1,3-benzothiadiazole and monothiadiazole cycloadducts, the yields of which were dependent upon the ortho substituent of I and molar ratios. Redn. of compd. II with SnCl_2 in AcOH-HCl gave the imidazolyl-thiazole III, while redn. with Sn in HCl gave tetra-aminobiphenyl I ($\text{R} = \text{R}_1 = \text{R}_2 = \text{NH}_2$) (IV), which was diazotized to give the corresponding bitriazolyl. IV, when heated in phosphoric acid, gave 1,8-diaminocarbazole in 27% yield from the dibromobiphenyldiol I ($\text{R} = \text{OH}$, $\text{R}_1 = \text{R}_2 = \text{Br}$).

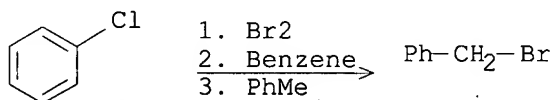
L36 ANSWER 7 OF 9 CASREACT COPYRIGHT 2003 ACS

RX(64) OF 95 - 2 STEPS



REF: Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry (1972-1999), (5), 893-6; 1984

RX(89) OF 95 - 3 STEPS

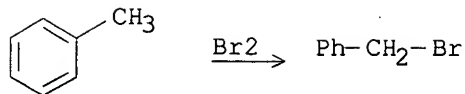


REF: Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry (1972-1999), (5), 893-6; 1984

AN 101:129889 CASREACT
 TI Photochemical bromination of simple arenes
 AU Bolton, Roger; Bhanger, Muhammad Iqbal; Williams, Gareth H.
 CS Dep. Chem., R. Holloway Coll., Egham, TW20 0EX, UK
 SO Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry (1972-1999) (1984), (5), 893-6
 CODEN: JCPRB4; ISSN: 0300-922X
 DT Journal
 LA English
 AB Photochem. bromination of PhR ($\text{R} = \text{H}$, F , Cl , CMe_3 , CF_3) and (in CCl_4) Ph_2 and C_{10}H_8 gave substitution and addn. products. The photodecompn. of 1,2,3,4,5,6-hexabromocyclohexane and the analogous PhCl adduct gave the parent arene, monobrominated halobenzene, and Br , which was scavenged by PhMe or C_6H_6 to give PhCH_2Br and PhBr or $\text{C}_6\text{H}_4\text{Br}_2$, resp. The addn. is kinetically controlled, so the mechanism of aryl bromide formation is largely through reversible adduct formation. This is consistent with the unusual orientation of the apparent attack by Br on the arene substrates, since the relative amts. of the isomeric aryl bromides are due to the relative stabilities and ease of HBr and Br_2 elimination. The range of isomer distribution is consistent with 2 competing processes involved in the formation of the aryl bromides, one of which may be the direct homolytic substitution of Br atoms on the arene.

L36 ANSWER 8 OF 9 CASREACT COPYRIGHT 2003 ACS

RX(1) OF 42



REF: Zhurnal Organicheskoi Khimii, 19(12), 2630; 1983

AN 100:138318 CASREACT

TI Effect of the 1-adamantyl substituent on homolytic bromination of toluenes

substituted in the ring

AU Rakhimov, A. I.; Ozerov, A. A.; Litinskii, A. O.

CS Volgogr. Politekh. Inst., Volgograd, USSR

SO Zhurnal Organicheskoi Khimii (1983), 19(12), 2630

CODEN: ZORKAE; ISSN: 0514-7492

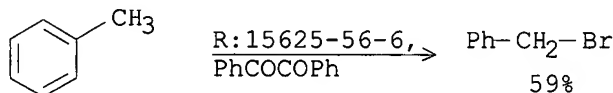
DT Journal

LA Russian

AB The relative rate consts. for bromination of 4-RC₆H₄R₁ (I; R = 1-adamantyl; R₁ = Me, CH₂Br, CHBr₂) with respect to I (R = H; same R₁) were 3.29, 2.24, and 1.77, resp. These values were too high to fit an LFER with σ_{para} , which was obeyed by several other I (R = 1-adamantyl).

L36 ANSWER 9 OF 9 CASREACT COPYRIGHT 2003 ACS

RX(2) OF 4



REF: J. Org. Chem., 28(11), 3256-8; 1963

NOTE: Classification: Bromination; # Conditions: Me₄NBr₃; (PhCO₂)₂; Rf 15mn

AN 60:16224 CASREACT

TI Brominating properties of tetramethylammonium tribromide

AU Avramoff, Moshe; Weiss, Judith; Schachter, Ozjasz

CS Weizmann Inst. Sci., Rehovoth, Israel

SO J. Org. Chem. (1963), 28(11), 3256-8

CODEN: JOCEAH; ISSN: 0022-3263

DT Journal

LA Unavailable

AB Treatment of Me₄NBr with Br in AcOH according to Chattaway and Hoyle (CA 17, 1949) gave Me₄NBr₃ (I), m. 118.0-18.5.degree., contg. 50.9% active Br and acting as a mild brominating agent. The action of I was investigated on several aromatic hydrocarbons capable of undergoing either nuclear or benzylic bromination. The hydrocarbon (0.01 mole) in 20 ml. C₆H₆ contg.

a

catalytic amt. of Bz₂O₂ was stirred to cessation of HBr evolution at 20.degree. with 0.01 mole I, the colorless Me₄NBr dissolved by addn. of H₂O, and the org. layer worked up (method A). The hydrocarbon (0.01

mole)

and 0.01 mole I in 30 ml. AcOH was refluxed until the Br color disappeared

or no more HBr was evolved (method B). The direction of the substitution was controlled by varying the nature of the reaction medium. In C₆H₆

contg. Bz2O2, PhMe, fluorene, and 1- and 2-methylnaphthalenes underwent benzylic bromination. Bromination of 2,6-Ac(MeO)C10H7 gave 2,6-BrCH2CO(MeO)C10H6. In AcOH, even in the absence of a catalyst, regular aromatic substitution occurred. Bromination of 1-MeC10H6 in AcOH with I gave 2,1-BrMeC10H6, in contrast to the 4,1-BrMeC10H6 obtained on bromination with Br in AcOH. The bromination of PhMe with I in AcOH was anomalous. PhMe (0.01 mole) and 0.02 mole I, refluxed 15 min. with a trace of Bz2O2 yielded 59% PhCH2Br, b. 194-8.degree.. PhMe (35 ml.), 13.85 g. anhyd. FeCl3, and 21.55 g. I stirred 6 hrs. at 60.degree.

yielded

72% p-BrC6H4Me, b. 184-6.degree.. Bromination of cyclohexene with (CH2CO)2NBr yielded 80-90% 3-bromocyclohexene, but in the presence of alkylammonium halides the yield was decreased and an appreciable amt. of 1,2-dibromocyclohexane (II), b40 134-6.degree., was produced. In contrast, bromination by I by either method A or B gave 86 and 78%

yields,

resp., of II only. The data indicate that I is highly dissocd. in polar solvents and the liberated Br mol. undergoes heterolytic fission in an ionic reaction, such as the aromatic substitution observed. In non-polar solvents in the presence of free radical initiators, I presumably undergoes homolytic fission to perform free-radical reactions such as benzylic substitution.

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